

EFFECT OF UNRESOLVED STRUCTURES ON THE LINE WIDTH IN ELECTRONIC PARAMAGNETIC RESONANCE

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Submitted to JETP editor September 21, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 1101-1105 (April, 1961)

The electronic paramagnetic resonance line width in solid paramagnetic salts is computed by taking into account the unresolved fine and hyperfine structures.

1. A single resonance line is usually observed in magnetically concentrated paramagnetic salts of elements of the first transition group. Fine and hyperfine splittings, which appear in dilute samples in the form of corresponding structures, are not resolved in the case of concentrated specimens because of the strong exchange interaction. Similarly, in magnetic dipole-dipole interactions they make their contribution to the width of the natural observed line and are also subject to the narrowing action of exchange. This fact, which is used to explain the divergence between experiment and theories which take into account only the dipole splitting of the magnetic resonance line,^{1,2} has been little studied quantitatively.

The equation for the absorption curve is derived below by the method suggested by Kubo and Tomita,³ taking into account the contribution of the unresolved fine and hyperfine structures in solid magnetically concentrated salts of elements of the first transition group.

2. Kubo and Tomita³ have shown that the spectral density $I(\omega)$ of the absorption line in magnetic resonance is determined by the Fourier transform of the autocorrelation functions $G(t)$ of the component of the magnetic moment along the applied alternating magnetic field

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t) e^{-i\omega t} dt, \tag{1}$$

where

$$G(t) = \langle \{ \hat{M}_x(t) \hat{M}_x \} \rangle. \tag{2}$$

Here the symmetrized product $\{ \hat{M}_x(t) \hat{M}_x \}$ is averaged with the density matrix, which can be replaced by a constant for not very low temperatures ($kT \gg \hbar\omega$). $\hat{M}_x(t)$ is the magnetization operator in the Heisenberg representation

$$\hat{M}_x(t) = \exp(it\hat{\mathcal{H}}/\hbar) \hat{M}_x \exp(-it\hat{\mathcal{H}}/\hbar), \tag{3}$$

where $\hat{\mathcal{H}}$ is the Hamiltonian of the system in the absence of the alternating field.

On consideration of the effects of motion and exchange, the Hamiltonian $\hat{\mathcal{H}}$ splits into two parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \hat{\mathcal{H}}', \tag{4}$$

such that $\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 = \hat{\mathcal{H}}_0$ is the unperturbed Hamiltonian defining the basis functions and $\hat{\mathcal{H}}'$ is the perturbation, whence

$$[\hat{\mathcal{H}}_1, \hat{\mathcal{H}}_2] = [\hat{\mathcal{H}}_2, \hat{M}_x] = 0. \tag{5}$$

Solving the equation of motion $i\hbar \dot{\hat{M}}_x(t) = [\hat{M}_x(t), \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}']$ by the method of successive approximations, we obtain an expansion of $G(t)$ in a series:

$$G(t) = \sum_{n=0}^{\infty} G_n(t), \tag{6}$$

the first three terms of which describe the basic characteristics of the effect of motion and exchange on magnetic resonance, according to which we can establish $G(t)$ in the form

$$G(t) = \sum_{\alpha} \langle | \hat{M}_{x\alpha} |^2 \rangle \times \exp \left\{ i\omega_{\alpha} t - \sum_{\gamma} \sigma_{\alpha\gamma}^2 \int_0^t (t-\tau) d\tau \exp(i\omega_{\gamma}\tau) f_{\alpha\gamma}(\tau) \right\}, \tag{7}$$

with accuracy which is sufficient for our purposes; here $\sigma_{\alpha\gamma}^2$ is the second moment of the broadening perturbation

$$\sigma_{\alpha\gamma}^2 = \langle | [\hat{M}_{x\alpha}, \hat{\mathcal{H}}'_{\gamma}] |^2 \rangle / \langle | \hat{M}_{x\alpha} |^2 \rangle, \tag{8}$$

$f_{\alpha\gamma}(\tau)$ is the correlation function:

$$f_{\alpha\gamma}(\tau) = \langle \{ [\hat{M}_{x\alpha}, \hat{\mathcal{H}}'_{\gamma}(\tau)] [\hat{\mathcal{H}}'_{-\gamma}(0), \hat{M}_{x,-\alpha}] \} \rangle / \langle | [\hat{M}_{x\alpha}, \hat{\mathcal{H}}'_{\gamma}(0)] |^2 \rangle. \tag{9}$$

The quantities $\hat{M}_{x\alpha}$, $\hat{\mathcal{H}}'_{\gamma}(t)$, ω_{α} , and ω_{γ} are defined by the relations

$$\begin{aligned} \exp [it\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2/\hbar] \hat{M}_x \exp [-it(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)/\hbar] \\ = \exp (it\hat{\mathcal{H}}_1/\hbar) \hat{M}_x \exp (-it\hat{\mathcal{H}}_1/\hbar) = \sum_{\alpha} \hat{M}_{x\alpha} \exp (i\omega_{\alpha}t), \end{aligned} \quad (10)$$

$$\begin{aligned} \exp [it(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)/\hbar] \hat{\mathcal{H}}' \exp [-it(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)/\hbar] \\ = \exp (it\hat{\mathcal{H}}_2/\hbar) \left[\sum_{\gamma} \hat{\mathcal{H}}'_{\gamma} \exp (i\omega_{\gamma}t) \right] \exp (-it\hat{\mathcal{H}}_2/\hbar) \\ = \sum_{\gamma} \hat{\mathcal{H}}'_{\gamma}(t) \exp (i\omega_{\gamma}t). \end{aligned} \quad (11)$$

3. For the description of the behavior of the lowest spin levels of a system of N identical magnetic ions of a solid paramagnetic salt, the Hamiltonian $\hat{\mathcal{H}}$ is introduced:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_z + \hat{\mathcal{H}}_{\text{fs}} + \hat{\mathcal{H}}_{\text{hfs}} + \hat{\mathcal{H}}_{\text{ss}} + \hat{\mathcal{H}}_e, \quad (12)$$

where we have the operators $\hat{\mathcal{H}}_z$ = Zeeman energy, $\hat{\mathcal{H}}_{\text{fs}}$ = fine structure, $\hat{\mathcal{H}}_{\text{hfs}}$ = hyperfine structure, $\hat{\mathcal{H}}_{\text{ss}}$ = magnetic dipole-dipole interaction, and $\hat{\mathcal{H}}_e$ = exchange interaction.

The local electric field at the position of location of the magnetic ion is frequently a combination of a strong field of cubic symmetry and a weak field of lower, usually axial, symmetry.⁴ Then

$$\hat{\mathcal{H}}'_z = -\Delta g\beta H \sum_k [\hat{S}_{zk} (\cos^2\vartheta_k - \frac{1}{3}) + \frac{1}{3} (\hat{S}_{+k} \exp(-i\varphi_k) + \hat{S}_{-k} \exp(i\varphi_k)) \sin\vartheta_k \cos\vartheta_k],$$

$$\hat{\mathcal{H}}'_{\text{fs}} = \hbar D \sum_k \left[(\hat{S}_{zk}^2 - \frac{1}{3} S(S+1)) - [\hat{S}_{zk}^2 - \frac{1}{4} (S_+ S_- + S_- S_+)]_k \sin^2\vartheta_k + \frac{1}{4} [(\hat{S}_z \hat{S}_+ + \hat{S}_+ \hat{S}_z)_k \exp(-i\varphi_k) \right.$$

$$\left. + (\hat{S}_z \hat{S}_- + \hat{S}_- \hat{S}_z)_k \exp(i\varphi_k) \right] \sin\vartheta_k \cos\vartheta_k + \frac{1}{4} [\hat{S}_{+k}^2 \exp(-2i\varphi_k) + \hat{S}_{-k}^2 \exp(2i\varphi_k)] \sin^2\vartheta_k,$$

$$g = \frac{1}{3} (g_{\parallel} + 2g_{\perp}), \quad \Delta g = g_{\parallel} - g_{\perp}, \quad \hat{S}_{\pm k} = \hat{S}_x \pm i\hat{S}_y. \quad (17)$$

The exchange forces are relatively short range and are effective only in salts with rather high concentrations of magnetic ions. Therefore, in a sufficiently magnetically concentrated salt, $\hat{\mathcal{H}}_z + \hat{\mathcal{H}}_{\text{fs}} + \hat{\mathcal{H}}_{\text{hfs}} + \hat{\mathcal{H}}_{\text{ss}}$ can be regarded as a perturbation relative to $\hat{\mathcal{H}}_{0z} + \hat{\mathcal{H}}_e$, i.e.,

$$\hat{\mathcal{H}}_1 = \hat{\mathcal{H}}_{0z}, \quad \hat{\mathcal{H}}_2 = \hat{\mathcal{H}}_e, \quad \hat{\mathcal{H}}' = \hat{\mathcal{H}}'_z + \hat{\mathcal{H}}'_{\text{fs}} + \hat{\mathcal{H}}'_{\text{hfs}} + \hat{\mathcal{H}}'_{\text{ss}}. \quad (18)$$

Experimentally, this corresponds to the case of observation of a single line of electron paramagnetic resonance without resolution of any structure.

It can be shown that the contributions to the spectral density $I(\omega)$ (1) from the different parts of the perturbation $\hat{\mathcal{H}}'$ (18) can be computed separately. The effect of exchange $\hat{\mathcal{H}}_e$ does not appear on this part of the width of the absorption peak, which is associated with the anisotropic part of the Zeeman energy (since $[\hat{\mathcal{H}}'_z, \hat{\mathcal{H}}_e] = 0$), and the term $\hat{\mathcal{H}}_z$ will be omitted in the consideration of exchange narrowing in solid salts.

$$\hat{\mathcal{H}}_z = -g_{\parallel}\beta \sum_k \hat{S}_{zk} \hat{H}_{zk} - g_{\perp}\beta \sum_k (\hat{S}_{xk} H_{xk} + \hat{S}_{yk} H_{yk}), \quad (13)$$

$$\hat{\mathcal{H}}_{\text{fs}} = \hbar D \sum_k [\hat{S}_{zk}^2 - \frac{1}{3} S(S+1)]. \quad (14)$$

For simplicity, we shall take the operators $\hat{\mathcal{H}}_{\text{hfs}}$ and $\hat{\mathcal{H}}_e$ to be isotropic:

$$\hat{\mathcal{H}}_{\text{hfs}} = \hbar A \sum_k \hat{S}_k \hat{I}_k, \quad \hat{\mathcal{H}}_e = \hbar \sum_{i>j} J_{ij} \hat{S}_i \hat{S}_j,$$

$$\hat{\mathcal{H}}_{\text{ss}} = g^2 \beta^2 \sum_{i>j} r_{ij}^{-3} [\hat{S}_i \hat{S}_j - r_{ij}^{-2} (\hat{S}_i r_{ij}) (\hat{S}_j r_{ij})]. \quad (15)$$

Here D and A are constants of the fine and hyperfine structures, $J_{ij} = J_{ji}$ = exchange integral, and r_{ij} = distance between the i-th and j-th magnetic ions.

Introducing the angles ϑ_k and φ_k , which are formed by the axis z'_k of the local field at the kth magnetic ion with the laboratory system of axes xyz ($z \parallel H$), we can represent $\hat{\mathcal{H}}_z$ and $\hat{\mathcal{H}}_{\text{fs}}$ in the form

$$\hat{\mathcal{H}}'_z = \hat{\mathcal{H}}_{0z} + \hat{\mathcal{H}}'_z, \quad \hat{\mathcal{H}}_{0z} = -g\beta H \sum_k \hat{S}_{zk} = -\hbar\omega_z \sum_k \hat{S}_{zk}, \quad (16)$$

We can represent the correlation function $f_{\alpha\gamma}(\tau)$ of the exchange motion in the form³

$$f_e(\tau) = \exp(-\frac{1}{2}\omega_e^2 \tau^2), \quad (19)$$

where ω_e = exchange frequency.

In the case of strong exchange $\langle |\hat{\mathcal{H}}'|^2 \rangle \ll \langle |\hat{\mathcal{H}}_e|^2 \rangle$, if we follow the scheme of Sec. 2 (for details see references 3 and 5), we obtain a Lorentz distribution for $I(\omega)$ with a half-width $\Delta\omega$:

$$\Delta\omega = \Delta\omega_{\text{fs}} + \Delta\omega_{\text{hfs}} + \Delta\omega_{\text{ss}}. \quad (20)$$

The dipole half-width $\Delta\omega_{\text{ss}}$ is known in general form.³ Therefore, we write down the explicit expressions only for $\Delta\omega_{\text{fs}}$ and $\Delta\omega_{\text{hfs}}$:

$$\begin{aligned} \Delta\omega_{\text{fs}} = (\pi/2)^{1/2} P\omega_e^{-1} [\xi_0^2 + (\xi_1^2 + \xi_{-1}^2) \exp(-\omega_e^2/2\omega_e^2) \\ + \xi_1 \exp(-2\omega_e^2/\omega_e^2)], \end{aligned} \quad (21)$$

where

$$\xi_0^2 = \frac{4}{5} N^{-1} \sum_k (1 - \frac{3}{2} \sin^2 \vartheta_k)^2,$$

$$\xi_1^2 = \frac{3}{2} \xi_{-1}^2 = \frac{4}{5} N^{-1} \sum_k \sin^2 \vartheta_k \cos^2 \vartheta_k,$$

$$\xi_2^2 = \frac{1}{5} N^{-1} \sum_k \sin^4 \vartheta_k, \quad P = D^2 [S(S+1) - \frac{3}{4}],$$

$$\omega_e^2 = 2J^2 S(S+1), \quad J^2 = N^{-1} \sum_{i \neq j} J_{ij}^2.$$

Here ϑ_k is the angle between the axis of the local electric field at the k th ion and the constant magnetic field H ; J^2 is the mean square of the exchange integral existing at a single ion. If the exchange takes place only with z nearest neighbors, then $J^2 = z \gamma^2$, where γ^2 is the mean square of the exchange integral for a pair of nearest neighbors.

For powders and supercooled liquids, the distribution of the axes of the local fields can be taken as isotropic in the mean; then

$$\begin{aligned} \Delta\omega_{fs} = & \frac{2}{15} (\pi)^{1/2} \left\{ \frac{D^2 [S(S+1) - 3/4]}{\sqrt{J^2 S(S+1)}} \right\} \\ & \times \left[\frac{3}{5} + \exp\left(-\frac{\omega_z^2}{4J^2 S(S+1)}\right) \right. \\ & \left. + \frac{2}{5} \exp\left(-\frac{\omega_z^2}{J^2 S(S+1)}\right) \right], \end{aligned} \quad (23)$$

The contribution $\Delta\omega_{hfs}$ of the isotropic hyperfine structure (15), in accord with reference 5, is equal to

$$\Delta\omega_{hfs} = \frac{1}{2} (\pi/3)^{1/2} \left[\frac{A^2 I(I+1)}{\sqrt{J^2 S(S+1)}} \right] \left\{ 1 + \exp\left[\frac{-3\omega_z^2}{4J^2 S(S+1)} \right] \right\}, \quad (24)$$

where I is the nuclear spin.

At frequencies $\omega_z^2 \leq J^2 S(S+1)$, the exponents in (21), (23), and (24) should be kept, while at frequencies $\omega_z^2 \gg J^2 S(S+1)$, they can be neglected.

This peculiarity of the frequency dependence of $\Delta\omega_{fs}$ and $\Delta\omega_{hfs}$ is completely analogous to the well-known "10/3 effect" in the theory of dipole broadening.^{1,5}

With the help of Eqs. (21) and (24) for monocrystals, and (23) and (24) for powders and supercooled liquids, we can estimate the part of the absorption line broadening due to unresolved structures.

We note that the contribution of the fine structure $\Delta\omega_{fs}$ (21) depends significantly on the angle ϑ and can be the reason for the occasional observance of anisotropy of line width in monocrystals. Since, in the single crystals of CrCl_3 , at a frequency of 37,000 Mc, the line width at $\vartheta = 0$ and $\vartheta = 90^\circ$ is given respectively by $\Delta H_{||} = (140 \pm 5)$ oe and $\Delta H_{\perp} = (98 \pm 3)$ oe.⁶ We estimate the exchange integral from the well-known relation of the theory of the molecular field $3k\Theta = 2JzS(S+1)$. The Curie temperature Θ for CrCl_3 is 27°K , $z = 6$.⁸ It suffices to set $D = 0.1 \text{ cm}^{-1}$, in order to obtain $2(\Delta\omega_{||} - \Delta\omega_{\perp}) = 38.3$ oe from Eqs. (21), (22).

Thus, from systematic measurements of the electron paramagnetic resonance line width, we can estimate the value of the fine and hyperfine splittings, even if the corresponding structures are not resolved.

The author thanks S. A. Al'tshuler for direction and constant attention to the work, and B. M. Kozyrev for discussion of the results.

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